RUBBER–THERMOPLASTIC COMPOSITIONS. PART I. EPDM–POLYPROPYLENE THERMOPLASTIC VULCANIZATES*

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INTRODUCTION

Thermoplastic elastomers are rubbery materials which can be fabricated by techniques usually associated with thermoplastic resins. Classical elastomers rely upon the crosslinked network, developed during vulcanization, to provide the retractive forces of rubber type elasticity. Thermoplastic elastomers contain rubber domains and resinous thermoplastic domains. The thermoplasticity results from the melting characteristics of the hard thermoplastic phase, while the rubber properties arise from the rubbery domains. Thermoplastic elastomers are, therefore, almost by definition, heterogeneous in their phase morphology. Such materials can be blends or block polymers. In the case of block polymers, the rubbery phase is not crosslinked chemically. However, hard or resinous phase domains occur as the hard segments of the block polymer which separate from the composition by agglomeration during cooling from the molten state. These domains act both as well-bonded reinforcing filler particles and as crosslinks. This is, of course, because the hard blocks are connected to the soft or rubbery segments by primary chemical bonds. In the case of the blend compositions, the hard and soft domains are separate polymeric species. However, there must be some form of interaction between the domains if useful properties are to be realized.

Recently, uncured or partially cured EPDM rubber has been blended with polyolefin resin to make thermoplastic elastomer-like compositions[1-4]. However, these compositions suffer deficiencies in performance as well as in certain aspects of fabricability. Only poor to fair performance at temperatures above 70°C in air or in oil has been achieved with the uncured to partially cured compositions. More recently, it has been found in our laboratories that fully cured EPDM compositions which are fabricable as thermoplastics can be prepared[5]. Such compositions, referred to here as thermoplastic vulcanizates, have superior strength, high-temperature mechanical properties, hot oil and solvent resistance, better compression set, etc. This report outlines critical parameters associated with these unique materials.

EXPERIMENTAL

PREPARATION OF THERMOPLASTIC VULCANIZATES BY DYNAMIC VULCANIZATION

The preparation of thermoplastic resin compositions containing vulcanized rubber, by dynamic vulcanization, has been described by Gessler[6]. The pro-

cedure was later used by Fischer[1] to prepare compositions of partially cured EPDM polyolefins. Dynamic vulcanization differs from the more common static vulcanization in that vulcanization occurs during mixing or mastication of the composition being prepared. If enough of a thermoplastic resin is present in the molten state, as part of the composition being masticated, the mixture does not lose processability as a result of vulcanization. This is true even when the rubber is fully cured. Thus products, elastomeric in nature yet fabricable as thermoplastics, can be prepared. This occurs within a certain range of proportions of rubber and resin. In the resulting compositions, cured rubber particles appear to be dispersed in the resin. If enough rubber phase is present, particles may interfere with one another to give a somewhat continuous rubber phase.

In the present work, the following general recipe was used:

EPDM (Epsyn® 70A)	100
Polyolefin resin	X
Zinc oxide	5
Stearic acid	1
TMTD (tetramethylthiuram disulfide)	Y/2
MBTS (2-benzothiazyl disulfide)	Y/4
Sulfur	Y

where X, the number of parts by weight of polyolefin resin, and Y, the amount of sulfur, were varied. In some instances the EPDM rubber was in the form of an oil extended, filled masterbatch.

The resin, rubber, zinc oxide and stearic acid were mixed (rate, 100 rpm) in a Brabender mixer with the oil bath controlled at 180–190°C. Two to three minutes after melting of the resin, the accelerators, TMTD and MBTS, were added. After another one-half minute the sulfur was added. Curing then occurred and was indicated by an increase in mixing torque or consistency by the Brabender Plasticorder. The consistency generally then becomes constant, and then may drop somewhat. This change in consistency due to vulcanization is less apparent when a large amount of oil or resin or a small amount of curative is used. Nevertheless, mixing was continued without interruption for about two or three minutes after the maximum consistency was observed. The composition was then removed from the mixer, and while still molten, passed once through a cold roll mill to give a sheet about 2 mm thick. The sheet was cut into small pieces which were remelted and mixed for another two minutes in the Brabender. Again the mass was removed from the mixer and formed into a 2 mm thick milled sheet. The sheet was then cut and compression molded in a frame (1.6 mm thick) between plates in a platen press at 210°C, then cooled under pressure. Aluminum foil (0.25 mm thick) was used between the molded sheet and plates. This allowed the entire surface of the sheet to move from the plate as the mold cooled. Depressions in the surface of the molded sheet (shrink marks) were thus minimized. Appropriate test specimens were die cut from the molded sheet and used after at least 24 hours storage at room temperature.

PREPARATION OF COMPOSITION BY BLENDING POWDERED VULCANIZED RUBBER WITH POLYOLEFIN RESIN (STATIC VULCANIZATION)

Compositions were also prepared from rubber which had been press cured in the absence of resin. The general recipe was the same as for the composi-

tions prepared by dynamic vulcanization. Here the value of Y, the amount of sulfur, was two parts and X, the amount of polyolefin, was 67 parts per 100 parts of ground rubber. Enough rubber for several batches was mixed on a roll mill at 70°C with the zinc oxide, stearic acid, sulfur and accelerators then press cured for 10 min at 200°C. Cured rubber was ground on a 70°C roll mill for various periods of time at mill nip settings to provide samples of various particle sizes. Each portion of powdered vulcanized rubber, of a certain average particle size, was then blended with polypropylene (Profax® 6723) in the Brabender at 100 rpm with the oil bath at 180–190°C. Mixing continued for about two minutes after the resin melted. The molten mass was passed through a roll mill to give a 2 mm thick sheet which was compression molded at 210°C as above.

DETERMINATION OF RUBBER PARTICLE SIZES IN THE THERMOPLASTIC VULCANIZATES

Rubber particle sizes were determined using an optical microscope. It was convenient to dilute the compositions, in the molten state, with butyl rubber. A dilution of about 1:50 enabled the observation (by transmission illumination) of the individual particles of rubber in thin, hot pressed (then cooled) sections of the dilution. A dilution was prepared by melt mixing about one gram of thermoplastic vulcanizate composition with 55 grams of butyl rubber in a Brabender mixer (oil, 180–190°C) for three to five minutes.

An optical microscope was used to determine the average diameters of about 200–250 cured rubber particles for each of the compositions prepared by blending powdered vulcanized EPDM with polypropylene resin. Number and weight averages were then recorded. The particles of dynamically vulcanized rubber were so small that their diameters could only be determined (visible light optical miscroscope) to be in the one to two micrometer range.

DETERMINATION OF CROSSLINK DENSITIES OF THE RUBBER PARTICLES

EPDM rubber compounds were statically cured for 10 min at 220°C in the absence of polyolefin resin, and swollen, in thin section (about 1.5 mm thick), for two days in cyclohexane at room temperature. The effective crosslink density ($\nu/2$) was then estimated by the Flory-Rehner equation[7]. The reported value[8] of 0.315 was the Huggins solubility parameter. Thus the crosslink density of rubber was estimated with rubber cured in the absence of polyolefin resin. This was necessary since the constraint of the rubber imposed by the polyolefin phase would greatly limit solvent swelling.

It may be argued that the presence of polyolefin might change the crosslink density, especially in the case of the dynamically cured compositions. However, we have determined that the polyolefin is essentially completely extractable from the cured rubber by boiling decalin or xylene. This would indicate there is little or no resin interaction with the curing system.

PROPERTIES OF THE COMPOSITIONS

The mechanical properties of the compositions were determined with test specimens depicted by ASTM procedure D-1708-66. However, the test procedure was somewhat modified. The specimens were pulled in a tensile tester at a crosshead speed of 2.5 cm per minute up to 30% elongation and then at 25 cm per minute until failure. Young's modulus (E), was estimated

TABLE I

PROPERTIES OF UNFILLED THERMOPLASTIC COMPOSITIONS

Composition number	Resin Type/parts per 100 parts of rubber (phr)[a]	Sulfur phr Y	Method of Prep.[c]	Crosslink density, $\nu/2$ "moles" $\times 10^5$ per ml of rubber	Rubber particle size, μm d_n	d_w	Shore D hardness	Young's modulus, MPa	Stress at 100% strain, MPa	Tens. str., MPa	Ult. elong., %	Tens. set, %
1	Polypropylene/66.7	2.0	S	16.4	72	750	43	97	8.2	8.6	165	—
2	Polypropylene/66.7	2.0	S	16.4	39	290	41	102	8.4	9.8	215	22
3	Polypropylene/66.7	2.0	S	16.4	17	96	41	105	8.4	13.9	380	22
4	Polypropylene/66.7	2.0	S	16.4	5.4	30	42	103	8.4	19.1	480	20
5	Polypropylene/66.7	2.0	D	16.4	about 1 to 2		42	58	8.0	24.3	530	16
6	Polypropylene/66.7	1.0	D	12.3	—		40	60	7.2	18.2	490	17
7	Polypropylene/66.7	0.5	D	7.8	—		39	61	6.3	15.0	500	19
8	Polypropylene/66.7	0.25	D	5.4	—		40	56	6.7	15.8	510	19
9	Polypropylene/66.7	0.125	D	1.0	—		35	57	6.0	9.1	407	27
10	Polypropylene/66.7	0.00	—	0.0	—		22	72	4.8	4.9	190	66
11	Polypropylene/33.3	1.00	D	12.3	—		29	13	3.9	12.8	490	7
12	Polypropylene/42.9	2.00	D	16.4	—		34	22	5.6	17.9	470	9
13	Polypropylene/53.8	2.00	D	16.4	—		36	32	7.6	25.1	460	12
14	Polypropylene[b]/81.8	2.00	D	16.4	—		43	82	8.5	24.6	550	19
15	Polypropylene/122	2.00	D	16.4	—		48	162	11.3	27.5	560	31
16	Polypropylene/233	5.00	D	14.5	—		59	435	13.6	28.8	580	46
17	None[b]/0.00	2.00	S	16.4	—		11	2.3	1.5	2.0	150	1
18	Polypropylene[b]/∞	0	—	—	—		71	854	19.2	28.5	530	—
19	Polyethylene/66.7	2.00	D	12.3	—		35	51	7.2	14.8	440	18
20	Polyethylene/66.7	0.0	—	0.0	—		21	46	4.1	3.5	240	24

[a] Polypropylene is Profax® 6723 and polyethylene is Marlex® EHM 6006.
[b] Compositions 17 and 18 control compositions purely of cured rubber or propylene.
[c] S = static; D = dynamic.

from the slope of the stress–strain curve near the origin (the "slow pulled" portion). From the rest of the stress–strain curve, the stress at 100% strain (M_{100}) the tensile strength (UTS) and ultimate elongation (UE) were determined.

The hardness of each composition was obtained by ASTM test method D2240-64T using a durometer. Hardness was observed after 5 seconds of presser foot contact. Tension set was determined with straight specimens by ASTM D412-66. Specimens measuring about $1.8 \times 1.8 \times 50.8$ mm were stretched to a length of 10×16 mm for 10 minutes, then relaxed for 10 minutes.

The dependence of stiffness on temperature was determined with a torsion pendulum[9]. Stiffness was then reported as a dynamic Young's modulus, assuming a Poissons ratio of 0.5 ($E' = 3G'$). The size of each pendulum was selected to keep the period about constant at 1 Hz.

RESULTS AND DISCUSSION

Mechanical properties, hardness and tension set values for unfilled thermoplastic compositions are given in Table 1. The effect of the rubber particle size is illustrated by compositions 1–5. The first four compositions were prepared by blending powdered vulcanized rubber with polypropylene resin. Composition 5 and all the rest of the vulcanizates in Table 1 were prepared by the dynamic vulcanization method. Compositions number 5–10 illustrate the effect of the extent of cure. Compositions 11–16 along with 5 show the effects of polyolefin resin/rubber ratio. Compositions 17 and 18 are "homogeneous" controls while 19 and 20 demonstrate that polyethylene can be used as well as polypropylene.

The effects of particle size on mechanical properties are represented by Figure 1. This is a composite stress–strain curve constructed from the data associated with compositions 1–5. Each "X" denotes a stress and strain at rupture. From Figure 1, then, ultimate stress, ultimate strain and energy to break (area under curve from origin to an appropriate "X") are apparent.
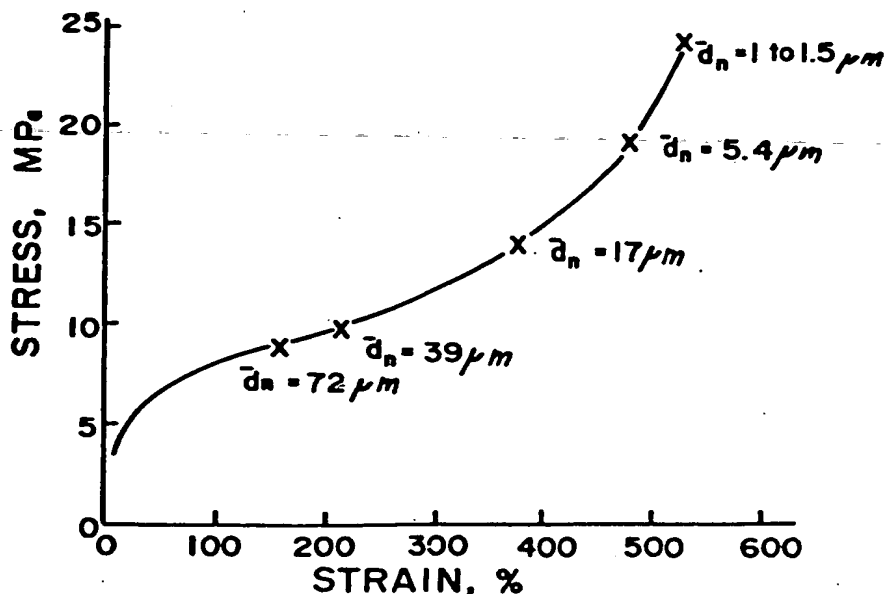

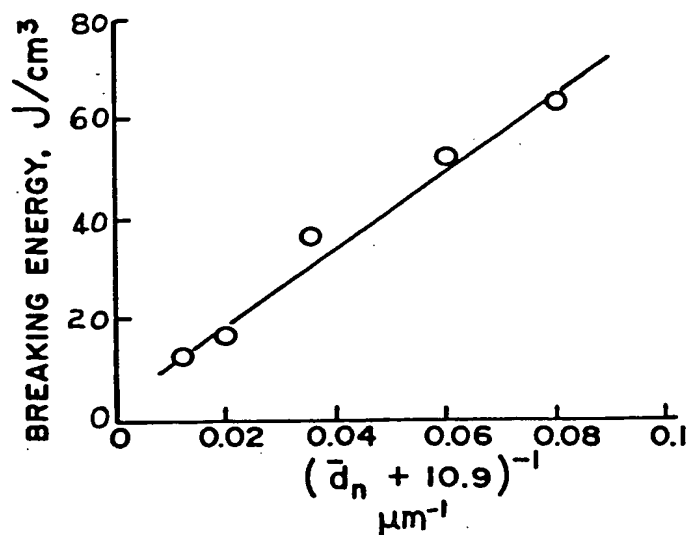FIG. 1.—Stress–strain relationship (X denotes failure).

FIG. 2.—The effect of rubber particle size on breaking energy.

The average rubber particle size associated with each "X" is noted. Clearly, the ultimate properties are an inverse function of rubber particle diameter. In Figures 2 and 3, ultimate tensile strength and energy to break are plotted against functions of the number average rubber particle size $\bar{d}_n$. The functions of $\bar{d}_n$ were selected with Griffith's theory of fracture in mind. The theory relates ultimate properties to size of material flaws and has been considered for elastomers by Gent[10] and others. Here an assumption is made that the material flaw sizes are proportional to the size of the rubber particles. Strength appears to be inversely proportional to the square root of the sum of the diameter and a constant. Energy to break is inversely proportional to the first power of the sum of the diameter and a constant. In each case, it is felt that the constant is indicative of an inherent flaw size
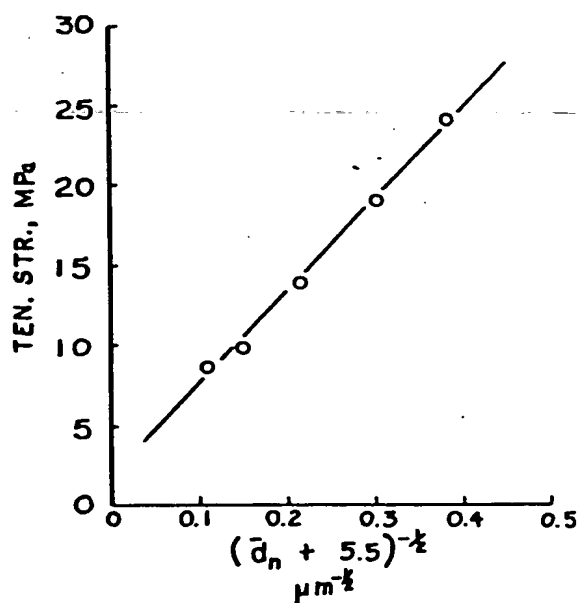

FIG. 3.—The effect of rubber particle size on tensile strength.

associated with the polypropylene. It should be noted, however, that in the cases of strength and energy, the constants for best fit were somewhat different (5.5 μm vs. 10.9 μm). It is interesting that an inherent flaw size of similar magnitude has been reported[10] for natural rubber.

Major effects of change in the extent of vulcanization or crosslink density ($\nu/2$) are given by Figure 4. Only a small amount of vulcanization is required for a large improvement in tension set. Tensile strength improves rather continuously as the crosslink density of the rubber phase increases, but the compositions remain fabricable as thermoplastics even at high rubber crosslink densities. This is surprising in view of earlier work[1]. However, only small changes in the stiffness of the compositions occur with great changes in the extent of cure. Young's modulus can even *decrease* slightly as a result of vulcanization. The improved strength could arise from a more favorable micromorphology which may be associated with more highly crosslinked rubber particles. More study will be necessary to explain in detail the reasons for the improvement in strength which accompanies increases in crosslink density.

Effects on composition properties due to changes in resin/rubber ratio are given in Figures 5 and 6. As the amount of polypropylene resin per amount of rubber increases, the compositions become less like rubber and more like a plastic resin. Modulus, hardness, tension set and strength increase. The shape of the plot of strength against the proportion of polypropylene is interesting. Strengths are low until at least 30 parts of resin per 100 parts of rubber (phr) are used. Then as the proportion of resin is further increased, strength rapidly increases until about 50 phr of the polyolefin is used. Further increases in the amount of resin can increase the strength only slightly. Thus, with only about 50 phr of polypropylene, a strength of about 25 MPa is obtained. This is about two and one-half times the expected average strength. In Table 1, only maximum tensile strengths are given. The pure resin, polypropylene, exhibits yield; provided they contain no more than about 75% resin, the thermoplastic vulcanizates

FIG. 4.—The effect of crosslink density on tensile strength and tension set.

FIG. 5.—The effect of resin content on properties of thermoplastic vulcanizates.

do not yield. The reported strength for pure polypropylene (28.8 MPa) is the maximum at yield. The strength at break for the pure polypropylene is only about 17 MPa. With this in mind, the strength behavior of the compositions is quite surprising.

FIG. 6.—The effect of resin/rubber ratio on Young's modulus.

Values of Young's modulus are plotted in Figure 6. The points are experimental and the solid line is calculated from the relationship[11]:

$$M = \phi_H{}^n(n\phi_s + 1)(M_U - M_L) + M_L,$$

where ϕ_H is the volume fraction of hard phase (resin) and ϕ_s is the volume fraction of soft phase (rubber). M_U and M_L are upper and lower bound Young's moduli:
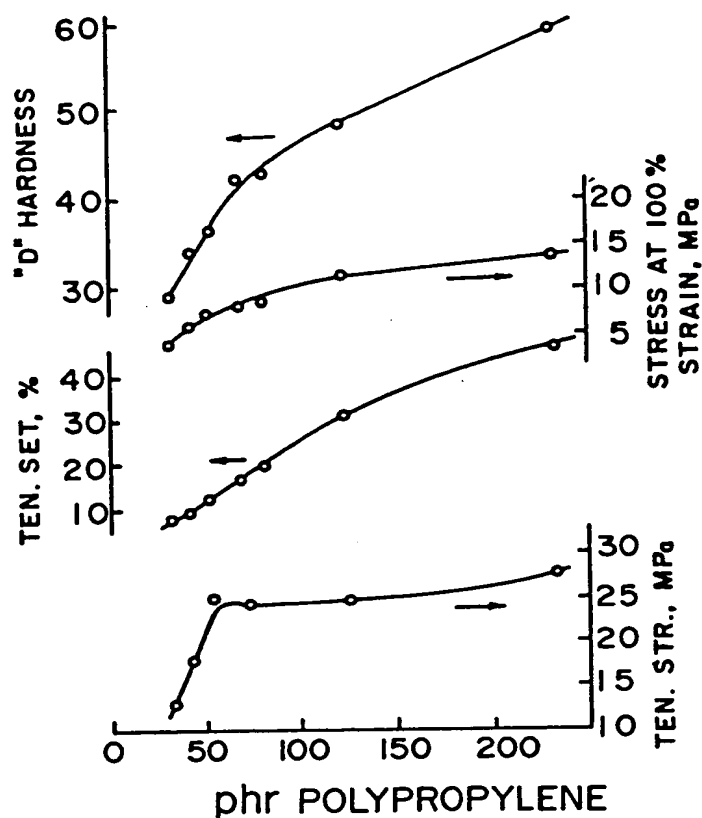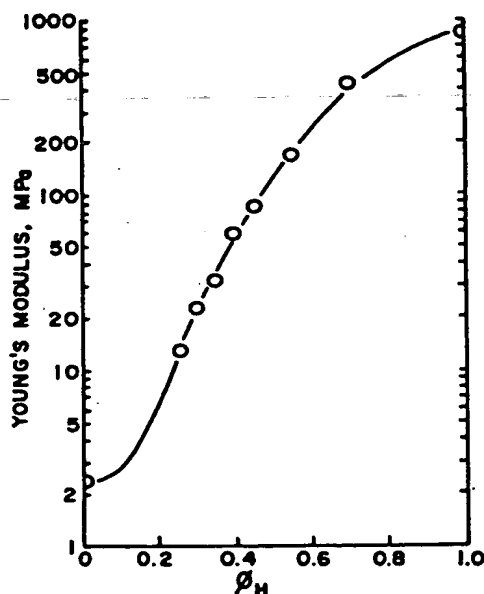
$$M_U = \phi_H M_H + \phi_s M_s,$$

and

$$M_L = (\phi_H/M_H + \phi_s/M_s)^{-1}.$$

In the case of this work, the parameter n has a value of about 3.1. This contrasts a previous value of 2 for unvulcanized blends of EPDM and polypropylene[12]. A change in micromorphology resulting from dynamic vulcanization of the blends might thus be indicated.

Dynamic modulus as a function of temperature is given by Figure 7. The composition is the same as no. 5 in Table 1. The effect of vulcanizing the rubber phase is to prevent a complete loss of elasticity and strength at the melting point of the resin phase. The vulcanized composition continues to exhibit sufficient strength for measurements of modulus by the torsion pendulum even after melting. In addition, the change in stiffness, throughout the temperature range of measurement is less in the vulcanized composition. The unique performance of the thermoplastic vulcanizates even above their melting points will indicate a variety of high temperature applications.

The data of Table 2 demonstrate the effects of black loading and oil extension (to soften the composition but also to make it weaker). The compositions are variations of no. 15 in Table 1. The effect of the filler is to strengthen the composition somewhat with some stiffening in respect to hardness and stress at 100% strain, but not in respect to the "zero strain" tangent Young's modulus. Both oil extension and carbon black loading can give compositions of lower cost but excellent quality.

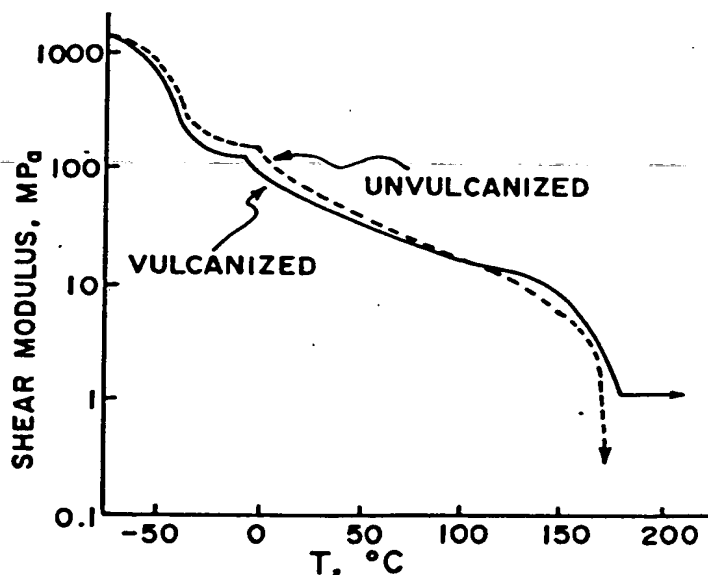It has been found that oil extended, filled compositions can be prepared

FIG. 7.—The effect of temperature on stiffness.

TABLE II

EFFECT OF CARBON BLACK AND EXTENDER OIL[a]

Carbon black, phr	Extender oil, phr	Tensile str., MPa	Stress at 100% strain, MPa	Young's modulus, MPa	Ult. elong., %	Shore hardness	Tension set, %
0.0	0.0	27.5	11.3	162	560	48D	31
80.0	0.0	31.0	14.3	120	410	51D	30
0.0	80.0	15.2	6.4	47	550	29D	19
80.0	80.0	23.0	7.2	23	530	33D	16
80.0	160.0	15.2	4.8	11.5	490	74A	13

[a] Carbon black is N327, and oil is Sunpar® 2280.

which are thermoplastics but perform quite well with respect to such properties as hot oil resistance, compression set, fatigue life, strength, etc. Compositions of this type can be fabricated by standard thermoplastic processes such as high speed injection molding, extrusion, calendering or vacuum forming. Thus the concept of thermoplastic vulcanizates has led to compositions having cured rubber properties, yet being fabricable as thermoplastics.

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RUBBER-THERMOPLASTIC COMPOSITIONS. PART V. SELECTING POLYMERS FOR THERMOPLASTIC VULCANIZATES*

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INTRODUCTION

Thermoplastic elastomeric materials have become important because they have many properties of vulcanized rubbers but can be rapidly fabricated as thermoplastics. Such materials can be block copolymers or they can be blends comprising rubber–plastic combinations.

Thermoplastic elastomers based on EPDM rubber and polypropylene were described in the first report of this series[1]. Such compositions, represented as dispersions of very small, fully-vulcanized particles of EPDM Rubber in polypropylene, were prepared by dynamic vulcanization (rubber cured during mixing with molten plastic). Similarly prepared compositions based on nitrile rubber and nylon resins were described in the second report of the series[2].

In the last report of this series[3], additional thermoplastic vulcanizates (TPV's) were described. Tough TPV compositions were obtained when the rubber and plastic had similar surface energies and when the plastic phase was crystalline. However, the considerations were limited to 12 compositions based on 3 types of rubber and 4 types of hard thermoplastic resin. Nevertheless, the success of that work has led to an expanded analysis. In the work reported here, approximately 100 thermoplastic vulcanizate compositions, based on 9 kinds of thermoplastic resin and 11 kinds of rubber, were considered.

The goal was to define the practical scope of the TPV concept in respect to the selection of rubber–plastic combinations. This was accomplished by an analysis which related mechanical properties of the TPV compositions to characteristics of the rubber and plastic components. It was done in much the same way as described in the previous report[3]; however, many more data were available for use. As a result, it is felt that a high degree of confidence in the conclusions is warranted.

EXPERIMENTAL

Compositions were prepared as before[1-3] by melt mixing the plastic, rubber and other components in a Brabender or Haake mixer. Generally, the plastic, rubber and other components of the composition, except for curatives, were mixed at controlled elevated temperatures (Table I) for about 2-6 min during which time the plastic melted and a blend was formed with the rubber. After blend formation, curatives were added to crosslink the rubber, and mixing was continued until a maximum consistency or mixing torque was observed.

TABLE I

MIXING AND MOLDING TEMPERATURES

Plastic	Stock mixing temp., °C	Molding temp., °C
Polypropylene (PP)[a]	185–190	210
Polyethylene (PE)[b]	160–180	210
Polystyrene (PS)[c]	170–190	210
Acrylonitrile-butadiene-styrene polymer (ABS)[d]	170–190	210
Polystyrene-co-acrylonitrile (SAN)[e]	170–190	210
Polymethyl methracrylate (PMMA)[f]	170–180	210
Poly-tetramethylene terephthalate (PTMT)[g]	220–230	250
Nylon 6,9 (PA)[h]	210	220
Polycarbonate (PC)[i]	200–220	250

[a]Profax® 6723.
[b]Marlex® EHM6006.
[c]Lustrex® HH101 or Dylark® 232.
[d]Lustran® 740 or Lustran 246.
[e]Lustran® DN52, DN57 or DN77.
[f]Lucite® 147.
[g]Tenite® 6P20A.
[h]Vydyne® 60H.
[i]Melron® M40F.

Each composition was removed from the mixer and then remixed for an additional minute in the molten state, to insure uniformity of the mixture. Molding was done in a frame mold. Temperatures for mixing and molding (Table I) depend on the plastic used. More details for mixing and molding appear in previous reports[1-3]. All compositions contained 60 parts of rubber per 40 parts of plastic. The rubber and plastic components are identified in Tables II and III. The abbreviations for the plastics are defined in Table I. The abbreviations for the rubbers are standard (ASTM D 1418); in addition, PTPR is poly-*trans*-pentenamer rubber, EVA is poly(ethylene-co-vinyl acetate) and CPE is chlorinated polyethylene rubber. Curatives and stabilizers of Table IV and Table V are used according to Table VI.

The mechanical properties of the compositions were determined with test specimens described by ASTM procedure D 1708-66. However, the test procedure was somewhat modified. The specimens were pulled in a tensile tester at a crosshead speed of 2.5 cm/min up to 30% elongation and then at a crosshead speed of 25 cm/min until failure. Young's modulus (E), was estimated from the slope of the stress–strain curve near the origin (the "slow pulled" portion). From the rest of the stress–strain curve, the stress at 100% strain, tensile strength σ_B and ultimate elongation ϵ_B were determined. Tension set (ASTM D 412-66) ϵ_S was determined by stretching 51 mm long specimens to 102 mm for 10 minutes then by measuring set after 10 minutes relaxation.

RESULTS AND DISCUSSION

Results of testing (tensile strength σ_B, ultimate elongation ϵ_B and tension set ϵ_S) are given in Tables VII, VIII and IX. Young's modulus and stress at 100% strain, though measured, are not considered here; the selection of polymers (rubber-plastic combinations) is based largely on the development of ultimate strength properties and elastic recovery. Stiffness related properties such as hardness, Young's modulus and stress at 100% strain are determined mainly by the

TABLE II

IDENTIFICATION OF RUBBERS[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	Polysar Butyl 301								
EPDM	Epsyn® 70A	Nordel® 1470	Epsyn® 70A						
PTPR	TPR 3-80 (Bayer)								
NR	SMR5								
BR	Cis-4 1203								
SBR	SBR 1502								
EVA	Ethylene Vinyl Acetate (50/50)								
ACM	Elaprim® AR153			Cyanocryl® R	Elaprim® AR153				
CPE	CMO136	CMO342							
CR	Neoprene W			Neoprene WRT	Neoprene W		Neoprene WRT	Neoprene W	
NBR	Hycar® 1092-30	Hycar 1094-80	Hycar 1092-80	Hycar 1032-80	Hycar 1092-30	Hycar 1053	Hycar 1092-80	Hycar 1000 × 88	Chemigum® 365

[a] Each composition is identified corresponding to a rubber-plastic (row-column) combination. There are 11 rubbers (rows) and 9 plastics (columns) which give 9 × 11 = 99 combinations. Abbreviations for plastics are defined in Table I. Abbreviations for rubbers are standard (ASTM D 1418); in addition PTPR is poly-trans-pentenamer (Bayer), EVA is ethylene-vinyl acetate copolymer rubber, and CPE is chlorinated polyethylene rubber.

TABLE III
IDENTIFICATION OF PLASTICS[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	Profax 6723	Marlex EHM6006	Lustrex HH101	Lustran 740	Lustran DN57	Lucite 147	Tenite 6P20A	Vydyne 60II	Melron M-101
EPDM			Dylark 232	Lustran 246	Lustran DN52				
PTPR			Lustrex HH101	Lustran 740	Lustran DN77				
NR			Dylark 232		Lustran DN57				
BR									
SBR									
EVA					Lustran DN52				
ACM			Dylark 232		Lustran DN77				
CPE									
CR			Lustrex HH101		Lustran DN57				
NBR									

[a] See footnote to Table II.

TABLE IV

CURATIVES

Curative system number	Curative components, phr
1	SP1045[a], 8.0; ZnO, 1.0
2	SP1056[b], 15.0; ZnO, 5.0
3	SP1056, 2.5; ZnO, 1.25
4	SP1056, 5.0; ZnO, 2.5
5	SP1056, 10.0; ZnO, 1.0
6	SP1056, 10.0; ZnO, 2.0
7	SP1056, 10.0; ZnO, 2.0; stearic acid, 1.0
8	SP1056, 10.0; ZnO, 3.0
9	SP1056, 10.0; ZnO, 5.0
10	SP1056, 5.0; ZnO, 1.0; $SnCl_2 \cdot 2H_2O$, 0.5
11	SP1056, 10.0; ZnO, 2.0; $SnCl_2 \cdot 2H_2O$, 1.0
12	HVA-2[c], 1.0
13	HVA-2, 1.11
14	HVA-2, 2.0
15	HVA-2, 2.83
16	HVA-2, 3.0
17	HVA-2, 3.2
18	HVA-2, 4.17
19	HVA-2, 5.0
20	HVA-2, 8.33
21	HVA-2, 4.0; MBTS[d], 1.0
22	HVA-2, 5.0; MBTS, 1.0
23	HVA-2, 5.0; MBTS, 1.25
24	HVA-2, 5.0; MBTS, 2.0
25	HVA-2, 6.0; MBTS, 1.5
26	HVA-2, 6.7; MBTS, 1.0
27	HVA-2, 6.9; MBTS, 1.4
28	HVA-2, 7.5; MBTS, 1.5
29	HVA-2, 7.5; MBTS, 3.0
30	HVA-2, 8.0; MBTS, 2.0
31	HVA-2, 8.35; MBTS, 1.67
32	HVA-2, 1.5; Vulcup® R,[e] 1.25; MgO, 1.5
33	HVA-2, 1.5; Vulcup R, 2.5
34	HVA-2, 1.5; Vulcup R, 2.5; MgO, 1.5
35	HVA-2, 2.5; Vulcup R, 2.5
36	HVA-2, 1.5; L-101[f], 1.25; MgO, 1.5
37	HVA-2, 2.0; L-101, 1.0
38	HVA-2, 3.0; L-101, 0.5
39	HVA-2, 3.0; L-101, 1.5
40	HVA-2, 4.0; L-101, 0.5
41	L-101, 1.25
42	L-101, 0.8; TAC[g], 0.8
43	L-101, 1.25; TAC, 1.5; MgO, 1.5
44	L-101, 1.0; SR351[h], 1.2
45	L-101, 0.5; SR351, 2.0
46	L-101, 1.0; SR351, 2.0
47	L-101, 0.5; SR351, 4.0
48	L-101, 1.0; SR351, 4.0
49	L-101, 3.0; SR351, 4.0
50	Sulfur, 2.0; MBTS, 0.5; TMTD[i], 1.0; ZnO, 5.0; stearic acid, 1.0
51	Sulfur, 2.0; MBTS, 0.5; TMTD, 1.0; ZnO, 5.0; stearic acid, 3.0
52	Sulfur, 2.0; MBTS, 0.75; TMTD, 1.5; ZnO, 5.0; stearic acid, 2.0
53	Sulfur, 0.75; Santocure[j], 2.5; ZnO, 2.5; stearic acid, 1.0
54	Sulfur, 1.5; Santocure, 5.0; ZnO, 5.0; stearic acid, 1.0
55	Tetrone A[k], 0.5; potassium stearate, 4.0
56	Sulfur, 1.0; TMTM[l], 1.0; DOTG[m], 1.0; ZnO, 5.0; stearic acid, 0.5
57	Sulfur, 1.0; TMTD, 1.0; DPG[n], 1.0; ZnO, 5.0; MgO, 4.0
58	Sulfur, 0.3; C-50[o], 5.0; stearic acid, 2.0

[a]Alkylphenol–formaldehyde resin, Schenectady Chems.
[b]Bromomethylolated and methylolated alkylphenol–formaldehyde resin, Schenectady Chems.
[c]N,N'-m-Phenylenedimaleimide, du Pont.
[d]2,2'-Benzothiazyl disulfide.
[e]α,α'-bis(t-butylperoxy)diisopropylbenzene, Wyrough and Loser.
[f]2,5-Dimethyl-2,5-bis(t-butyl peroxy)hexane, Pennwalt.
[g]Triallyl cyanurate, Cyanamid.
[h]Trimethylolpropane triacrylate, Sartomer.
[i]Tetramethylthiuram disulfide.
[j]N-cyclohexyl-2-benzothiazole sulfenamide, Monsanto.
[k]Pentamethylenethiuram hexasulfide, du Pont.
[l]Tetramethylthiuram monosulfide.
[m]Di-o-tolylguanidine, Cyanamid, du Pont.
[n]Diphenylguanidine, Cyanamid, Monsanto.
[o]A soap blend for AR rubbers, Cyanamid.

proportions of rubber and plastic[1-3]. Though proportions of the rubber and plastic components have an effect on ultimate and recovery properties, problems generally arise from an inability to obtain elastomeric thermoplastic vulcanizate compositions of good integrity, regardless of the rubber–plastic proportions.

All of the compositions contained rubber and plastic in a weight ratio of 60/40. This ratio has been chosen for screening of rubber–plastic pairs since we have found that, when good compositions were obtained at the 60/40 rubber–plastic ratio, they were soft enough and elastic enough (tension set less than 50%) to be considered elastomeric.

The values of tensile strength σ_B are given in Table VII. The values in parentheses for CPE-PTMT, CR-PTMT and CR-PA are in doubt since the rubbers (CPE and CR) are insufficiently stable to withstand processing at the high melt temperatures for PTMT (polyester) and PA (nylon polyamide). The value for EVA-PTMT is in doubt because of the instability of the peroxide curative which was spent before complete mixture with the melt. EVA must be peroxide cured and no sufficiently stable peroxide curative is known for use at the high temperatures required for PTMT melt mixing. For similar reasons, other tensile

TABLE V

STABILIZER SYSTEMS

Stabilizer system	Stabilizer system components, phr
A	Flectol® H, 0.5
B	Flectol H, 0.83
C	Flectol H, 1.0
D	Flectol H, 2.0
E	Santoflex® 13, 1.0
F	Santoflex 13, 2.0
G	Advastab® TM-181, 1.0
H	Advastab TM-181, 2.0
I	MgO, 5.0
J	Mark 1589B, 0.3; Drapex 6.8, 5.0; DSTDP, 0.5; MgO, 2.0; Polygard, 0.5
K	Mark 1589B, 0.3; Drapex 6.8, 5.0; DSTDP, 0.5; MgO, 4.0
L	Flectol H, 1.0; Polygard, 0.5
M	Flectol H, 2.0; Polygard, 0.5
N	Polygard, 0.5
P	Drapex 6.8, 5.0; MgO, 10.0; lead stearate, 2.0

TABLE VI

CURATIVE AND STABILIZER USAGE[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	9	8	4	50	51	9	6	52	3
EPDM	50	50	37	50	37	5	38	39	20
PTPR	11	54	11	10	10	53	16 C	16 D	11
NR	2	22	27 B	26	26 C	31 D	23	25 D	28 F
BR	19	20	19 C	20	20 C	18 B	17	25 D	13 B
SBR	1	24	19 C	26 C	26 C	18 B	19	12 C	15
EVA	43 L	32 N	36 N	35	36	34 B	46	42	33
ACM	55	55	55	58 D	55	55	55	55	55
CPE	40 J	45	48 K	48 K	46	48 K	49 H	44 P	47 K
CR	57	56	31 B	22 I	22 I	57	19	(21 G)	—
NBR	36 L	29 B	41 M	46	41 M	14 A	E	12 C	30 D

[a]See footnote to Table II. Numbers in table correspond to curing systems of Table IV and letters correspond to stabilizer systems of Table V.

TABLE VII

TENSILE STRENGTH σ_B OF 60–40 RUBBER–PLASTIC THERMOPLASTIC VULCANIZATES[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	21.6	14.9	0.9	1.7	4.3	5.4	1.4	4.0	1.3
EPDM	24.3	16.4	7.9	3.2	5.6	6.0	12.2	7.7	15.7
PTPR	22.7	12.1	6.9	11.0	13.4	4.7	12.1	10.8	2.5
NR	26.4	18.2	6.2	5.8	8.4	1.8	10.9	5.7	6.7
BR	20.8	19.3	11.6	9.9	8.3	3.5	12.8	16.3	2.1
SBR	21.7	17.1	15.8	10.8	8.1	5.7	21.7	14.6	7.3
EVA	17.8	18.9	12.7	9.6	12.9	9.3	(3.4)	10.9	9.6
ACM	4.04	4.21	11.4	9.4	7.7	6.21	14.6	16.1	5.2
CPE	12.3	10.5	14.0	13.7	17.9	17.0	(13.0)	17.3	20.8
CR	13.0	13.8	15.5	12.8	12.5	8.9	(13.5)	(3.2)	14.7
NBR	17.0	17.6	7.7	13.6	25.8	10.8	19.3	21.5	18.2

[a]Values are in MPa; see footnote to Table II.

TABLE VIII

ULTIMATE ELONGATION ϵ_B OF 60-40 RUBBER–PLASTIC THERMOPLASTIC VULCANIZATES[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	380	312	3	18	7	6	156	34	161
EPDM	530	612	69	18	5	6	102	30	66
PTPR	210	280	35	15	10	10	47	60	5
NR	390	360	85	56	14	58	62	42	21
BR	258	229	73	64	12	5	52	121	5
SBR	428	240	89	70	12	15	102	201	19
EVA	349	349	166	102	109	59	(126)	160	84
ACM	18	20	20	144	18	21	135	163	140
CPE	314	221	140	197	151	146	(159)	160	135
CR	144	390	67	96	7	5	(65)	(6)	94
NBR	204	190	20	164	196	56	350	320	130

[a] Values are in %; see footnote of Table II.

TABLE IX

TENSION SET OF 60-40 RUBBER-PLASTIC THERMOPLASTIC VULCANIZATES[a]

Rubbers	Plastics								
	PP	PE	PS	ABS	SAN	PMMA	PTMT	PA	PC
IIR	23	28	—	—	—	—	—	—	26
EPDM	16	—	—	—	—	—	—	—	—
PTPR	20	27	—	—	—	—	—	—	—
NR	24	—	—	—	—	—	—	—	—
BR	27	—	—	—	—	—	—	—	—
SBR	30	36	—	—	—	—	—	—	—
EVA	36	—	70	—	—	—	(—)	25	—
ACM	—	58	—	65	—	—	41	56	17
CPE	55	37	—	—	91	82	(40)	59	85
CR	33	—	—	—	—	—	(—)	(—)	—
NBR	31	—	—	—	55	—	25	44	—

[a] Values are in %; see footnote to Table II.

strength values may also be low; however, for the purposes of this work the parenthetic values were removed from consideration in attempts to correlate the measured properties of the rubber–plastic compositions with characteristics of the rubber and plastic components. Of course, the stability of each component in the presence of the others, in a system of conditions depending thereon, is in itself a characteristic expected to correlate with blend properties. It might be suggested that different polyesters and different nylons (of differing melting points) be used with rubbers of differing stabilities.

The values of ultimate elongation ϵ_B are given in Table VIII. Again, the parenthetic values are in doubt for the reasons stated above. The values of tension set are given in Table IX. Many values are missing because the measurement is impossible with poor compositions of insufficient extensibility. A few values are missing because the work was done over a period of years during which a testing protocol was evolving. Tension set was not measured on a few of the compositions (mostly ones containing PE) prepared early in our work.

The tension set value of 17% obtained for ACM–PC (acrylate rubber–polycarbonate) appears excessively low (high elastic recovery). Young's modulus was also extremely low, 1.9 MPa. It would appear that rubber is the only continuous phase, yet the composition is moldable as a thermoplastic. This could be explained if either the rubber did not cure in the presence of molten polycarbonate resin, or if the molten polycarbonate decomposed in the presence of the acrylate polymer, possibly by transesterification. For these reasons, the low tension set value was not used in the correlations with polymer component characteristics.

CHARACTERISTICS OF COMPONENT POLYMERS

The mechanical properties of the thermoplastic vulcanizates were correlated with parameters characteristic of the polymer blend components (rubber and plastic). The parameters are given in Table X. The method for estimating these characteristics and the rationale for the selection of each characteristic are discussed here.

Critical surface tension for wetting.—This parameter γ_c has been used as an estimate of polymer surface tension (surface energy). It was introduced by W. A. Zisman as a convenient measure of surface tension of a solid polymer[4]. Its estimation is based on the determination of contact angles of various liquids against a given polymer surface *vs.* the surface tensions of the liquids. The liquid surface tension corresponding to the extrapolated value of zero for contact angle θ (cos $\theta = 1.00$) is the critical surface tension for wetting (or spreading). It was believed that γ_c is approximately γ_s, the surface tension of the solid polymer. More recently[9], surface tensions of molten polymers have been determined at various temperatures, and estimates of γ_s were made by extrapolation to temperatures corresponding to the solid state of the polymers (glass, crystalline or semicrystalline).

Our purpose here was to compare the surface energies of the plastic and rubber phases. It was felt that such a comparison would enable a relative, though rough, estimate of interfacial tension between the rubber and plastic during melt mixing. Interfacial tension is a factor which determines, at least in part, the droplet size of one liquid dispersed in another[5]. The lower the interfacial tension, the smaller are the droplets. (Relative viscosities, proportions, time and tensity of mixing are other factors[6,7].) After dynamic vulcanization, the droplet size might well relate to the size of the vulcanized rubber particles dispersed in the plastic[3].

TABLE X

APPROXIMATE POLYMER[a] CHARACTERISTICS

	σG_H, MPa	E, MPa	γ_c^b	N_c^c	W_c^d
Polypropylene (PP)	30.0	660	28	—	0.63
Polyethylene (PE)	31.7	1218	29	—	0.70
Polystyrene (PS)	42	1550	33	—	0.00
ABS	58[e]	865	38	—	0.00
SAN	58	1730	38	—	0.00
Polymethylmethacrylate (PMMA)	61.8	1316	39	—	0.00
Polytetramethylene terephthalate (PTMT)	53.3	1322	39	—	0.31
Nylon 6,9 (PA)	46	850	39	—	0.25
Polycarbonate (PC)	66.5	1255	42	—	0.00
IIR	—	3	27	570	0.00
EPDM	—	3	28	460	0.00
Poly-trans-pentenamer (PTPR)	—	3	31	417	0.00
IR (NR)	—	3	31	454	0.00
BR	—	3	32	416	0.00
SBR	—	3	33	460	0.00
Ethylene-vinylacetate rubber (EVA)	—	3	34	342	0.00
ACM	—	3	37	778	0.00
Chlorinated polyethylene (CPE)	—	3	37	356	0.00
CR	—	3	38	350	0.00
NBR	—	3	39	290	0.00

[a] For identification of plastic see Table I, for rubbers see Table II.
[b] γ_c is critical surface tension for wetting, mN/m.
[c] N_c is critical molecular length of rubber molecules, number of chain atoms.
[d] W_c is wt. fraction of crystallinity.
[e] ABS was considered as SAN containing BR particles; thus ϵ_H for ABS was considered to be the same as for SAN. The somewhat increased rubber concentration (over 60 wt. %) should have only a small effect on ultimate properties.

The interfacial tension between two *monomeric* liquids is approximated by the difference between the two surface tensions[8] (Antonoff's Rule). However, this is not true for polymers[9,10]. Nevertheless, we have found a hypothetical surface tension γ_x, characteristic for each polymer listed in Wu's review of interfacial tension between molten polymers[9,10]; if the value γ_x for one polymer is subtracted from that of another polymer, the interfacial tension is estimated, with about 80% of the variation among the data points being explained (for measurements at 140°C). The hypothetical values γ_x correlate with γ_c.

It has been noted that γ_c correlates with solubility parameter[11-13]. It should further be noted that the difference between the solubility parameters of two polymers $|\delta_1 - \delta_2|$ is closely related to γ_{12}, the interfacial tension between the two polymers in the liquid state. Indeed, Helfand has given a theoretical basis for this[14].

Our conclusion from all of this is that $\Delta\gamma_c$, the difference between critical surface tensions for wetting of each of two polymers may be a qualitative estimate of γ_{12}, though the difference $|\gamma_1 - \gamma_2|$ between actual surface tension values does not correlate well with γ_{12}. The lower the difference $\Delta\gamma_c$, then, the smaller would be the particles of vulcanized rubber. Of course this is what was considered in the previous report of this series[3]. Further, the smaller the rubber particles, the greater would be the expected tensile strength σ_B and ultimate elongation ϵ_B. The effect of rubber particle size on properties of thermoplastic vulcanizates has been noted before[1].

As in the previous report, values of γ_c were taken from the literature[13]. Those

values which were not available were estimated on the basis of the correlation between solubility parameter δ and γ_c. For crystalline materials, the values were somewhat altered to relate to the molten state by allowing for expansion due to crystallite melting. However, the values corresponded to room temperature rather than the temperature of mixing. It was felt that the relative differences between γ_c values would not change much with temperature. The use of room temperature values was convenient since the literature values were from room temperature measurements.

Crystallinity.—The weight fraction of crystallinity W_c was again considered as it was in the previous report[3]. The reason was empirical for its consideration in that work, and it is considered here since its effect on strength properties was great. The values in Table X are approximations based on densities.

Tensile strength of the hard phase material.—Again, as in the previous work, the tensile strength of the hard phase material σ_H was considered; it represents a limit for the rubber–plastic blend. Yield stress was used as σ_H for crystalline materials rather than the stress at break, which occurs only after necking and drawing; generally, none of the rubber–plastic compositions exhibited neck-drawing behavior. The values used for σ_H of the blend components were determined in the same manner as for the rubber–plastic compositions, by using compression molded specimens which had been equilibrated against laboratory air. For nylon, many of the literature values for strength relate to dessicated specimens and are therefore somewhat higher than the values in Table X.

Critical entanglement spacing.—The critical entanglement spacing N_c is measured as the number of polymer chain atoms which corresponds to the molecular weight sufficiently large for entanglements to occur in the undiluted polymer. It has generally been measured as corresponding to the molecular weight where the slope of the plot of log viscosity *vs.* log molecular weight changes from 1.0 to about 3.4, the change being associated with intermolecular interference or entanglement. A polymer having a low value of N_c would have a high entanglement density and a high plateau modulus but a low value for the molecular weight between entanglements. N_c is approximately proportional to the molecular weight between entanglements[15,16]. Polymer molecules of relatively large cross-sectional area generally have high values for N_c; while "thin molecules", especially those which are at least somewhat polar, exhibit low N_c values[15,17-19].

When the data for ultimate elongation were first assembled into the "grid" represented by Table VIII, it was observed that better TPVs were produced from rubbers such as CPE and NBR (low N_c) than from the acrylate rubber (high N_c). As a result of this observation, correlations with N_c were attempted.

It has been observed that when polymers are blended, one with another, fibrous structures first appear which can then break up into droplets[6,20], in much the same way as droplets form from liquids of low viscosity during atomization from a simple jet nozzle[21]. It was more or less intuitively felt that polymer molecules which tend to mutually entangle might be drawn into finer "fibers", during the early phase of mixing, to give emulsions of droplets of smaller size. A similar intuition has been expressed in the postulation of a theory for ductility in amorphous materials[22].

Values of N_c for all of the rubbers, obtained under the same conditions, are not available in the literature. However, Aharoni has correlated N_c with the molecular weight per chain atom M_o/Z, where M_o is the molecular weight of a repeating polymer unit and Z is the number of polymer chain atoms per repeating unit[19]. He developed three correlations corresponding to "highly flexible poly-

mers", "polymers of intermediate flexibility" and "stiff backbone polymers";
these are given in corresponding order:

$$N_c = 275 + 10.5 \ (M_o/Z) \tag{1a}$$

$$N_c = 125 + 10.2 \ (M_o/Z) \tag{1b}$$

$$N_c = 0 + 5.35 \ (M_o/Z) \tag{1c}$$

The values of N_c used here were calculated from Equation (1a) for purely hy-
drocarbon rubber (IIR, EPDM, PTPR, IR, BR and SBR) and Equation (1b) was
used for EVA, ACM, CPE, CR and NBR. With copolymer rubbers, M_o/Z was
calculated as a weight average by assuming a "large" repeating unit containing
all of the monomer in appropriate proportions. Equation (1c) was not used.

CORRELATIONS BETWEEN COMPOSITION AND COMPONENT PROPERTIES

Stress at break.—The stress at break σ_B was treated as a relative strength σ_B/σ_H
since σ_H was believed to be a limiting factor; in other words, it was felt that high-
strength plastics could give high-strength thermoplastic vulcanizates[3]. The ratio
σ_B/σ_H was then related to $\Delta\gamma_{SH}$ (the difference $|\gamma_S - \gamma_H|$ between γ_c for the soft
phase and γ_c for the hard phase material), weight fraction crystallinity of the
plastic material W_c and the critical entanglement length N_c (expressed as the
number of chain atoms in the molecular length required for entanglement).
Multiple regression analysis gave the following equation:

$$\sigma_B/\sigma_H = 0.244 + 1.02 W_c - 0.000032(\Delta\gamma_{SH})N_c$$
$$- 0.0296(\Delta\gamma_{SH})W_c - 0.00076 N_c W_c. \tag{2}$$

The t-test values for the four coefficients were 7.40, 5.16, 2.93 and 3.16 for W_c,
$(\Delta\gamma_{SH})N_c$, $(\Delta\gamma_{SH})W_c$ and $N_c W_c$, respectively, and the equation explains 77.3% of
the variation in σ_B/σ_H ($r^2 = 0.773$), with 90 degrees of freedom for error. (Four
data points were not used for reasons stated above, relating to thermal stability.
Had these data been used, about 70% of the variation in σ_B/σ_H would have been
explained).

Though the equation is not the same as that obtained in the previous work[3],
the conclusions are confirmed. Strong, vulcanized blend compositions are ob-
tained from strong, crystalline plastics which are similar in surface energy to the
rubbers blended therewith. An additional conclusion is now possible because of
the use of additional rubbers in the experimental design. Thus, rubbers of lower
N_c (higher entanglement density) give stronger compositions. Higher entangle-
ment densities might enable greater drawing of rubber "threads" before breakup
during mixing (as stated above).

The effects of $\Delta\gamma_{SH}$, N_c and W_c on strength are illustrated, in part, by the
lower portion of Figure 1. The effect of one dependent variable is plotted with
the other two dependent variables held constant, each at a desirable level. The ef-
fects are only partially described by Figure 1 because Equation 2 contains inter-
actions, and the precise effect of one dependent variable depends on the values of
the other two dependent variables.

The agreement between values of σ_B/σ_H calculated from Equation (2) and
those experimentally observed is illustrated by Figure 2. This agreement
($r^2 = 0.773$) is not as good as that obtained for σ_B/σ_H in the previous report
($r^2 = 0.943$). However, that agreement[3] was obtained with only 9 degrees of free-
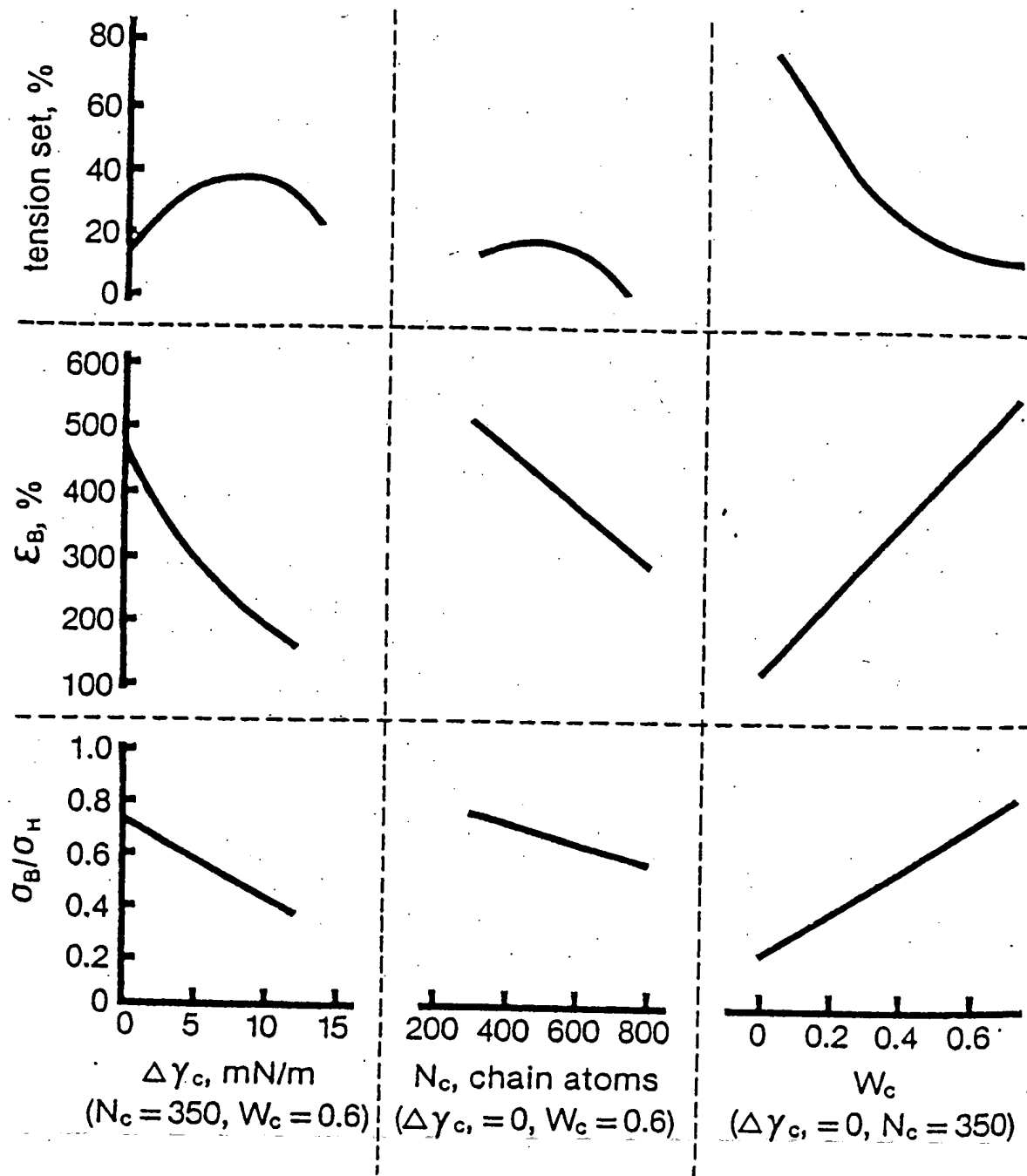dom for error. In other words, with more data (95 compositions *vs.* 12), more can

FIG. 1.—The effect of pure component characteristics on the properties of thermoplastic vulcanizate compositions. σ_B/σ_H is the relative tensile strength, ϵ_B is the ultimate elongation (%) and ϵ_S is the tension set (%). $\Delta\gamma_{SH}$ is the difference between the critical surface tension for wetting γ_c (mN/m) of the rubber and that of the plastic; N_c is the critical molecular length (chain atoms of rubber molecules) for entanglement; W_c is the weight fraction of crystallinity of the hard phase material.

go awry. Nevertheless, the present agreement is more significant because of the large number of data points.

Strain at break (ultimate elongation).—The strain at break ϵ_B varies also with $\Delta\gamma_{SH}$, N_c and W_c. The equation obtained for the regression is as follows (ϵ_B expressed in %):

$$\epsilon_B = 130.8 - 24.07\Delta\gamma_{SH} + 858.5W_c + 1.39(\Delta\gamma_{SH})^2$$
$$- 32.70(\Delta\gamma_{SH})W_c - 0.742N_cW_c. \quad (3)$$

FIG. 2.—The agreement between observed and calculated relative strengths.

The t-test values for the coefficients are 4.03, 10.49, 3.14, 4.82 and 5.06 for $\Delta\gamma_{SH}$, W_c, $(\Delta\gamma_{SH})^2$, $(\Delta\gamma_{SH})\,W_c$ and N_cW_c, respectively. The equation explains 79.0% of the variation in ϵ_B ($r^2 = 0.790$) with 89 degrees of freedom for error. Again compositions from crystalline plastic materials with surface-energy-matched rubbers of high entanglement density are the best. As for the strength data analysis, the effects are given, again only in part, in Figure 1. The agreement with experimental values is of about the same quality as for σ_B/σ_H, and the scattergram would look about the same as that for Equation (2), plotted in Figure 1. The discussion under "stress at break" (above) applies here.

Tension set.—Tension set ϵ_S (inverse measure of elastic recovery) can also be expressed as a function to the $\Delta\gamma_{SH}$, N_c, W_c. In the equation, ϵ_S is in %.

$$\epsilon_S = -0.2125 + 0.297N_c - 127.9W_c - 0.3441(\Delta\gamma_{SH})^2 - 0.000197N_c^2$$
$$+ 146.7W_c^2 + 9.148(\Delta\gamma_{SH})\,W_c - 0.1926N_cW_c. \quad (4)$$

The t-test values for the coefficients are 1.32, 2.00, 4.23, 1.04, 2.40, 4.07 and 1.35 for N_c, W_c, $(\Delta\gamma_{SH})^2$, N^2, W_c^2, $(\Delta\gamma_{SH})\,W_c$ and N_cW_c, respectively. The equation explains 80.1% of the variation in tension set ($r^2 = 0.801$) with 20 degrees of freedom for error. It should be again noted that the EVA–PC data point was not used for reasons stated above. Had that data point been used, about 74% of the variation in ϵ_S would have been explained.

The effects are illustrated in part by the upper portion of Figure 1. An in-

crease in the surface energy difference $\Delta\gamma_{SH}$ or in the characteristic entanglement length N_c (of the rubber) can be associated with either an increase or decrease in tension set. Generally, a poor elastic recovery (high tension set) occurs at intermediate values of $\Delta\gamma_{SH}$ or N_c. On the other hand, an increase is the crystallinity (of the plastic material) is generally associated with better elastic recovery (lower tension set). In the previous work[3] the data were insufficient for the observation of curvature in the function of $\Delta\gamma$ (t-value is 4.23 for the square term). The effect of N_c was not observed, though its significance here is only of moderate confidence. The t-values for N_c, N_c^2 and $N_c W_c$ are only 1.32, 1.04, and 1.35, corresponding to p-values of about 0.2, 0.3 and 0.3, respectively; if the coefficients for the square and interaction terms are dropped, t for the coefficient of N_c becomes 1.42 (p = about 0.15), but r^2 for the equation drops from 0.801 to 0.780.

If we accept Figure 1 as an over-all view of the effects, certain conclusions can be drawn: (a) An increase in the crystallinity W_c of the plastic material component improves both mechanical integrity and elastic recovery. (b) Rubbers of higher entanglement densities (lower N_c) give compositions of greater mechanical integrity (higher strength and ultimate elongation). (c) Compositions, in
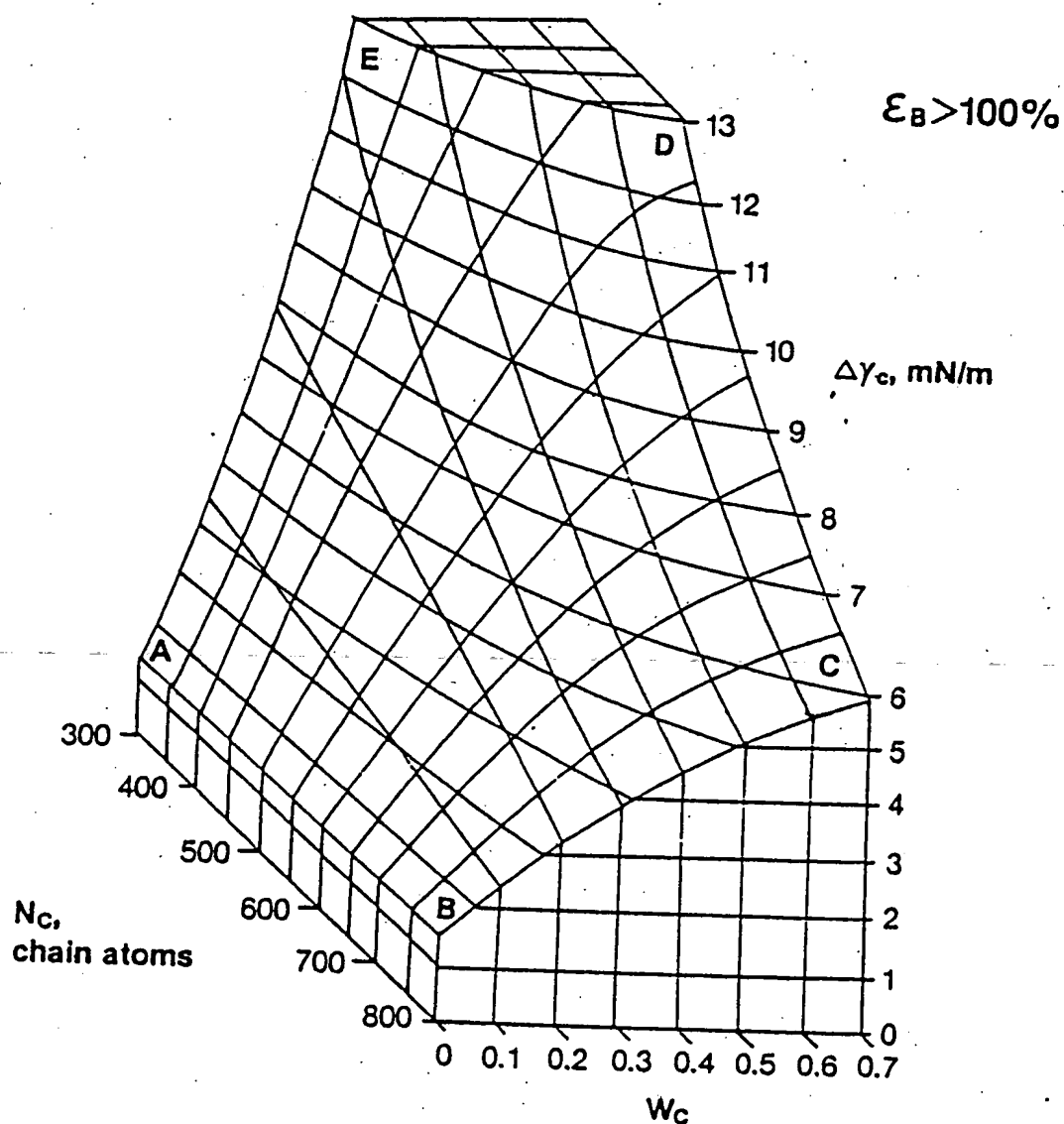

FIG. 3.—Pure component requirements for ultimate elongation $\epsilon_s > 100\%$. See Figure 1 caption for the definition of symbols.

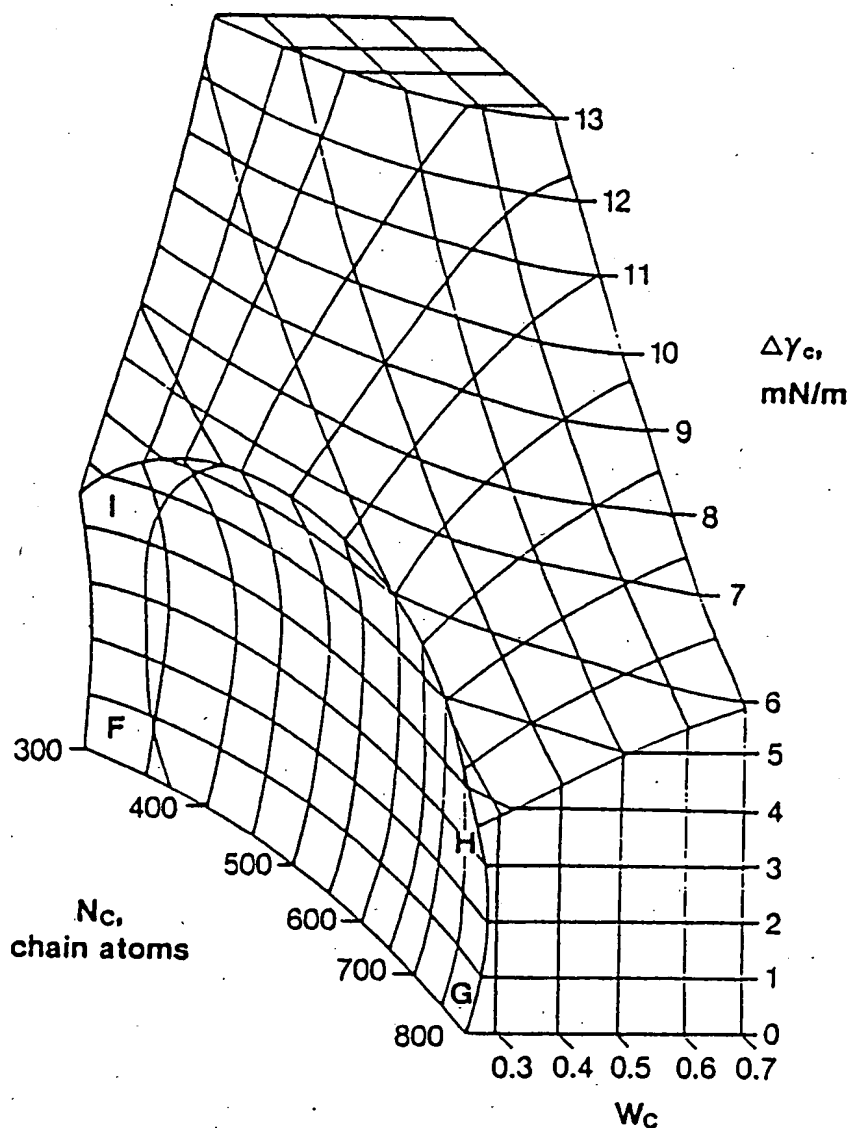$\varepsilon_B > 100\%$
ten. set $< 50\%$

FIG. 4.—Pure component requirements for ultimate elongation $\epsilon_s > 100\%$ and tension set $\epsilon_s < 50\%$. See Figure 1 for the definition of symbols.

which the surface energies of the rubber and plastic material are closely matched, are strong and extensible. As stated in the arguments presented above, and in the previous report, we feel that the matching of surface energies give lower interfacial tensions, which results in smaller rubber particles which act as smaller stress concentrator-flaws, thus the high strength and extensibility associated with lower values of $\Delta\gamma_{12}$.

SELECTING RUBBER-PLASTIC COMBINATIONS

A number of criteria could be considered in the identification of rubber-plastic combinations for thermoplastic vulcanizates. As well as the technological aspects, one might consider costs and availability of materials. Among the technological aspects, one might include processability, toxicology, in-plant asthetics, etc. However, for this report, economics and materials availability (which can

$\varepsilon_B > 200\%$

ten. set $< 50\%$

$\Delta\gamma_{SH}$, mN/m
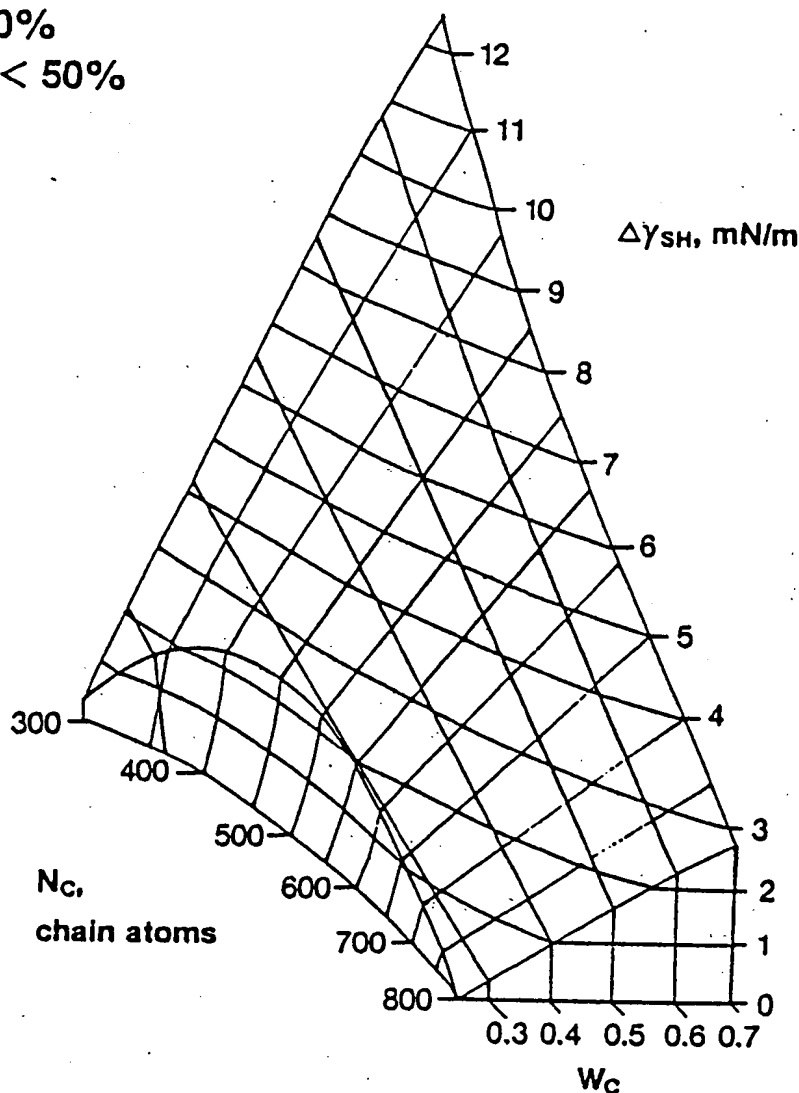
N_c, chain atoms

W_c

FIG. 5.—Pure component requirements for ultimate elongation $\epsilon_B > 200\%$ and tension set $\epsilon_s < 50\%$. See Figure 1 for definition of symbols.

change from time to time) and processing characteristics, etc. (which are subjects of product development, only after mechanical properties are demonstrated) will not be considered.

Only ultimate elongation ϵ_B and tension set ϵ_s will be considered. They are estimates of two primary attributes of an elastomeric material, e.g., mechanical integrity and elastic recovery. Strength might also be used; however, the changes in strength closely parallel the changes in ultimate elongation. Material attributes such as thermal-oxidative stability, hot oil resistance, temperature-use range, fabricability, etc., can only be considered after the demonstration of adequate mechanical properties. The ϵ_B and ϵ_s criteria, however, are only a preliminary screen.

If it is decided that only an ultimate elongation ϵ_B of 100% is required, a wide range of rubber-plastic combinations would be adequate. This is illustrated by Figure 3 which is a plot according to Equation (3) for $\epsilon_B = 100\%$. Each point on the surface ABCDE, plotted in dimensions of N_c, W_c, and $\Delta\gamma_c$ corresponds to a 60/40 rubber-plastic thermoplastic vulcanizate which exhibits a calculated ϵ_B value of 100%. Thus compositions, represented by points falling below the ABCDE surface, within the hypothetical "solid" structure give calculataed ϵ_B

$\varepsilon_B > 300\%$
ten. set $< 30\%$
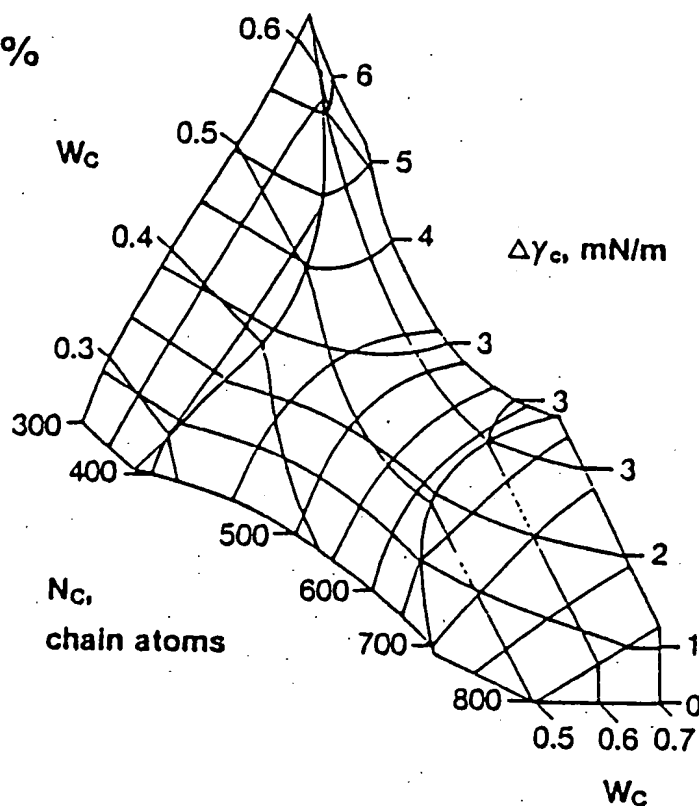
FIG. 6.—Pure component requirements for ultimate elongation $\epsilon_B > 300\%$ and tension set $\epsilon_s < 30\%$. See Figure 1 for definition of symbols.

values greater than 100%. This would embrace about 45% of the compositions. If the experimentally measured values of ϵ_B are used, also about 45% of the rubber-plastic combinations gave ϵ_B value of 100% or more.

If we consider that a tension set of 50% or less is required, in addition to the requirement $\epsilon > 100\%$, then the hypothetical solid structure of Figure 4 is the calculated result. This time the surface, FGHI, calculated from Equation (4), for ϵ_s is superimposed. All compositions corresponding (in respect to the dimensions of N_c, W_c and $\Delta\gamma_{SH}$) to points on the surface FGHI correspond to compositions giving calculated ϵ_s values of 50%. Compositions corresponding to the intersection of the FGHI surface with the ABCDE surface of Figure 3 (the curved line HI) have calculated values of $\epsilon_s = 50\%$ and $\epsilon_B = 100\%$. For compositions corresponding to points within the hypothetical "solid" structure of Figure 4, calculated $\epsilon_s < 50\%$ and calculated $\epsilon_B > 100\%$. About one-third of the compositions give calculated values of ϵ_B and ϵ_s which meet these criteria. Of course, these criteria are still loose enough to include many compositions of only marginal value.

If we limit our considerations to compositions in which $\epsilon_B > 200\%$ and $\epsilon_s < 50\%$, the hypothetical "solid" structure of Figure 5 is constructed on the basis of Equations (3) and (4). Only about one-quarter of the compositions fall within the structure of Figure 5, according to the calculations. These compositions would be expected to have fairly useful properties.

An even more severe limitation results in the structure of Figure 6, which corresponds to calculated values such that $\epsilon_B > 300\%$ and $\epsilon_s < 30\%$. Less than 10% of the compositions are included. These are all based on the polyolefins (PP & PE) which, alone, are high enough in crystallinity.

If we adopt the criteria used in the case illustrated by Figure 5 ($\epsilon_B > 200\%$,

$\epsilon_S < 50\%$), it would appear that the hard, plastic material should be at least 15–30% crystalline. If the crystallinity W_c is minimal (15–30%), $\Delta\gamma_{SH}$ must be less than 0.5–3.0 mN/m, but with W_c as high as 0.6–0.7, $\Delta\gamma_c$ can be as high as 10–12 mN/m, but only if N_c is as low as 300–400 chain atoms. This rather complex situation is perhaps most clearly illustrated by Figure 5, itself.

CONCLUSIONS

Based on a few characteristics of the pure rubber and plastic components, rubber–plastic combinations can be selected, with a high probability of success, to give thermoplastic vulcanizates (by dynamic vulcanization) of good mechanical integrity and elastic recovery. The characteristics used in the selection are estimated surface energies, crystallinity of the hard phase (plastic) material and the critical chain length, of the rubber molecules, for entanglement. The best compositions are prepared when the surface energies of the rubber and plastic material are matched, when the entanglement molecular length of the rubber is low (high entanglement density) and when the plastic material is crystalline. Of course, it is required that neither the plastic, nor the rubber decompose in the presence of the other at temperatures required for melt mixing. Also, a curing system is required, appropriate for the rubber under the conditions of melt-mixing.

ACKNOWLEDGMENT

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THERMOPLASTIC POLYURETHANE ELASTOMER MELT POLYMERIZATION STUDY*

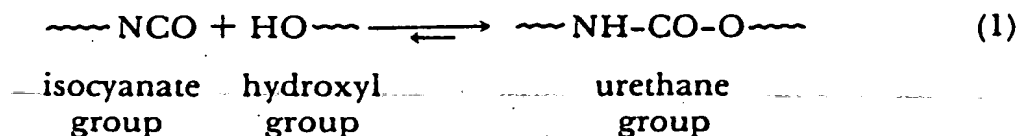C. S. SCHOLLENBERGER, K. DINBERGS, AND F. D. STEWART

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INTRODUCTION

Because of the relatively low volatility, good compatibility, high reactivity, and liquid or low-melting nature of their reactant components, polyurethanes can be produced readily in the melt by polyaddition, even at moderate temperatures and atmospheric pressure. Such polymerizability is attractive in that it enables the polymers to be formed quickly, efficiently, and in a relatively small space. There are no large solvent storage tanks to accomodate, no solvents nor reactants to recover and repurify for recycling, no contaminated water to clean before discharge, and no atmospheric pollution by gases or particulates to deal with. In an era of high capital costs, keen commercial competition, and worldwide concern for a clean environment, such a manufacturing process obviously has much to recommend it.

POLYMER FORMATION

In the formation of thermoplastic polyurethane elastomers, the reactants (diisocyanate, macroglycol, and small chain-extender glycol) join end-to-end to produce essentially linear polymer chains linked together through urethane groups, which are covalent and reasonably strong although the strength varies with structure.

$$\sim\!\!\sim\!NCO + HO\!\sim\!\!\sim \rightleftharpoons \sim\!\!\sim\!NH\text{-}CO\text{-}O\!\sim\!\!\sim \qquad (1)$$

isocyanate   hydroxyl   urethane
  group   group   group

The heat of reaction is reported to be -218 kJ/mol for the hexamethylene diisocyanate and 1,4-butanediol reaction[1]. The same diisocyanate, reacting with poly(ethylene adipate) glycol at 100°C has a reaction velocity constant, k, of 0.00083 $1 \cdot mol^{-1} \cdot s^{-1}$ with an activation energy, E, of 46.0 kJ/mol[2,4]. At the same temperature, diphenylmethane-4,4'-diisocyanate (MDI) reacts with poly-(diethylene adipate) glycol in chlorobenzene with $k = 0.00091$ $1 \cdot mol^{-1} \cdot s^{-1}$, and $E = 43.9$ kJ/mol[3,4].

As Equation (1) indicates, urethane formation is an equilibrium reaction with equilibrium constant K:

$$K = \frac{[NHCOO]}{[NCO][OH]} \qquad (2)$$